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CONTRACT N00014-81-C-0776

TASK No. NR 051-775

TECHNICAL REPORT #37

**CONTACT THEOREMS FOR MODELS OF THE STICKY ELECTRODE**

by

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Prepared for Publication in the Journal of  
Chemical Physics

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8 8 12 14 05 4

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #37	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Contact Theorems for Models of the Sticky Electrode		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) L. Blum, M.L. Rosinberg, and J.P. Badiali		8. CONTRACT OR GRANT NUMBER(s) N00014-81-C-0776
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of Puerto Rico Box AT, Río Piedras, P.R. 00931		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Code 472 Office of Naval Research Arlington, VA 22217		12. REPORT DATE 11-5-88
		13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)  unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; Distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES  Prepared for publication in the Journal of Chemical Physics		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Structured electrode, interface, <del>theory</del> sticky, electrodes. JES		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  A contact theorem for the interface between a hard, flat, smooth wall with an arbitrary distribution of sticky sites and a fluid containing charged hard spheres is derived.		

CONTACT THEOREMS FOR MODELS  
OF THE STICKY ELECTRODE

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## SUMMARY

A contact theorem for the interface between a hard, flat, smooth wall with an arbitrary distribution of sticky sites and a fluid containing charged hard spheres is derived.

In recent times there have been a number of experiments which reveal the detailed nature of the metal-electrolyte interface. It is then of interest, to incorporate the details of the surface structure into the theoretical models of the electrode interface<sup>(1)</sup>. A rather basic way of doing this is to use the sticky potential of Baxter<sup>(2)</sup>, which has been used to study adsorption phenomena at interfaces<sup>(3)</sup>. A model of a structured interface in which the atoms of the metallic electrode are represented by sticky sites was discussed in a previous publication<sup>(4)</sup>.

On the other hand, one knows that in spite of the relative complexity of the interactions at charged, flat interfaces, there is a sum rule, which derives from momentum conservation which is the so-called contact theorem<sup>(5)</sup> which relates the contact density near a hard wall to the excess charge on that wall. In the absence of image forces we have, for the primitive model, in which the ions are hard spheres of diameter  $\sigma_i$ , embedded in a continuum dielectric media.

$$k_B T \sum_{i=1}^s \rho_i(\sigma_i/2) = P + \frac{\epsilon E^2}{8\pi} \quad (1)$$

where  $\rho_i(\sigma_i/2)$  is the contact density of the ion  $i$  ( $i = 1 \dots s$ ),  $k_B$  is the Boltzmann constant,  $T$  the absolute temperature,  $P$  is the pressure,  $\epsilon$  the dielectric constant and  $E$  the external applied field. Equation (1) represents the force balance equation. For the non-primitive model in which the solvent is represented by a collection of hard spheres of diameter  $\sigma_n$  ( $n = 1 \dots M$ ) with an electric dipole (or in general, a multipole), the contact theorem (1) becomes

$$k_B T \sum_{i=1}^s \rho_i(\sigma_i/2) + k_B T \sum_{n=1}^M \rho_n(\sigma_n/2) = P + \frac{E^2}{8\pi} \quad (2)$$

where we have lost the dielectric constant  $\epsilon$  in the last term, and we got an extra term in the left hand side.

In the present note we extend the contact theorem (1) and (2) to the case in which the electrode wall has an arrangement of sticky spots represented by the interactions.

$$e^{-\beta v_i(\vec{r}_1)} = 1 + \lambda \delta(x_1) F(\vec{R}_1) \quad (3)$$

where  $\beta = 1/k_B T$  is the Boltzmann factor,  $v_i(\vec{r}_1)$  is the adsorption potential,  $\vec{r}_1 = x_1, y_1, z_1$  is the coordinate of particle 1,  $\vec{R}_1 = y_1, z_1$  is the position in the adsorbing plane, while  $x_1$  is the distance to that plane. For a regular lattice of adsorbing sites<sup>(4)</sup>,

$$F(\vec{R}_1) = \sum_{\vec{m}=\vec{m}_y, \vec{m}_z} \delta(\vec{R}_1 - \vec{R}_{\vec{m}}) \quad (4)$$

where  $\vec{R}_{\vec{m}}$  indicates the position of the sticky sites, indexed by the entire numbers  $\vec{m}_y, \vec{m}_z$ . But in general  $F(\vec{R})$  is an arbitrary function. The parameter  $\lambda$  is just an order parameter.

The number density of particles of species  $i$  at  $\vec{r}_1$  is  $\rho_i(\vec{r}_1)$ . We define the regular part of this function by means of the relation :

$$\rho_i(\vec{r}_1) = e^{-\beta v_i(\vec{r}_1)} y_i(\vec{r}_1) = y_i(\vec{r}_1) \left[ 1 + \lambda \delta(x_1) F(\vec{R}_1) \right] \quad (5)$$

Consider now the Born-Green-Yvon equation for a mixture near a planar interface :

$$\begin{aligned}
& k_B T \frac{\partial}{\partial x_1} \rho_i(\vec{r}_1) \\
& = y_i(\vec{r}_1) \lambda F_i(\vec{R}_1) \frac{\partial}{\partial x_1} \delta(x_1) - \rho_i(\vec{r}_1) \frac{\partial}{\partial x_1} u_i(x_1) \\
& - \rho_i(\vec{r}_1) \sum_j \int d\vec{r}_2 \rho_j(\vec{r}_2) g_{ij}(1,2) \frac{\partial}{\partial x_1} u_{ij}(r_{12}) \quad (6)
\end{aligned}$$

where  $u_i(x_1)$ ,  $u_{ij}(r_{12})$  are the 1 and 2 body forces,  $g_{ij}(1,2)$  is the inhomogeneous pair correlation function.

If we integrate (6) over  $\vec{r}_1$ , divide by  $S$ , the area of the interface and use the definitions :

$$\bar{\rho}_i(x_1) = \frac{1}{S} \int d\vec{r}_1 \rho_i(\vec{r}_1) \quad (7)$$

$$\bar{Y}_i(x_1) = \frac{1}{S} \int d\vec{R}_1 y_i(\vec{r}_1) F(\vec{R}_1) \quad (8)$$

we get, after a short calculation :

$$\begin{aligned}
& k_B T \sum_i \left[ \bar{\rho}_i(\infty) - \bar{\rho}_i(0) \right] = - \lambda \sum_i \frac{\partial}{\partial x} \bar{Y}_i(x) \Big|_{x=0} \\
& - \sum_i \int d\vec{r}_1 \rho_i(\vec{r}_1) \frac{\partial}{\partial x_1} u_i(x_1) \\
& - \frac{1}{S} \sum_{i,j} \int d\vec{r}_1 d\vec{r}_2 \rho_i(\vec{r}_1) \rho_j(\vec{r}_2) g_{ij}(1,2) \frac{\partial}{\partial x_1} u_{ij}(r_{12}) \quad (9)
\end{aligned}$$

and

$$k_B T \sum_i \bar{\rho}_i(0) = \lambda \sum_i \frac{\partial}{\partial x} \bar{Y}_i(x) \Big|_{x=0} + P - \frac{1}{S} \int d\vec{r}_1 \rho_i(\vec{r}_1) \frac{\partial}{\partial x} u_i(x) \quad (10)$$

where  $P$  is the bulk pressure. The last term depends on the explicit form of the wall particle interaction. For a flat, charged wall, we get using :

$$u_i(x) = e_i \times E_0 \quad (11)$$

where  $e_i$  is the charge, and  $E_0$  is the bare field at the surface. Using electroneutrality, we get, after a short calculation :

$$k_B T \sum_i \bar{\rho}_i(0) = \lambda \sum_i \frac{\partial}{\partial x} \bar{Y}_i(x) \Big|_{x=0} + P + \frac{\epsilon E_0^2}{8\pi} \quad (12)$$

which is the extension of the contact theorem<sup>(5)</sup> to a sticky surface with an arbitrary sticky potential  $\lambda F(\vec{R})$ . The new term can be put in a slightly more explicit form for a surface with a sticky point lattice (equation 4).

$$\lambda \sum_i \frac{\partial}{\partial x} \bar{Y}_i(x) \Big|_{x=0} = \frac{\lambda}{\omega} \sum_i \frac{\partial}{\partial x} y_i(x,0) \Big|_{x=0} \quad (13)$$

where we have assumed that the sticky point is at the origin of the lattice, and  $\omega$  is the area of the unit cell.

Equation (13) also applies to the case of a mixture of ions and hard solvent molecules, in which case the dielectric constant is  $\epsilon = \epsilon_0 = 1$  in the gaussian system.

The above procedure can be used to extend the contact theorem previously derived for an ideally polarizable interface<sup>(6)</sup>. The result is



(using the notation of Ref. 6, for the left (L) and right (R) phases) :

$$\begin{aligned}
 p^L - p^R &= \alpha^L \left[ \bar{\phi}(0) - \phi^L \right] - \alpha^R \left[ \bar{\phi}(0) - \phi^R \right] \\
 &+ k_B T \Sigma \left[ \bar{\rho}_i^L(-\sigma_i/2) - \bar{\rho}_i^R(\sigma_i/2) \right] \\
 &- k_B T \lambda \frac{\partial}{\partial x} \left\{ \Sigma \left[ \bar{Y}_i^L(-\sigma_i/2 - x) - \bar{Y}_i^R(\sigma_i/2 + x) \right] \right\}_{x=0} \quad (14)
 \end{aligned}$$

In a recent publication, F. Cornu<sup>(7)</sup> has verified these theorems for the case of the 2-dimensional one component plasma.

#### Acknowledgements

L. B. is supported by the Office of Naval Research. He also thanks Prof. P. Turq and Prof. B. Jancovici for their hospitality at the University of Paris, where part of this research was done. We thank Dr. F. Cornu for communicating her results prior to publication.

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